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Aeronautical Electronic and Electrical Laboratory

REPORT NO. NADC-EL-N6208

2 MAR 1962

TECHNICAL NOTE
URETHANE FOAMS FOR AEROSPACE APPLICATION

Dr. H. R. Moore



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U. S. NAVAL AIR DEVELOPMENT CENTER
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REPORT NO. NADC-EL-N6208 - TECHNICAL NOTE, URETHANE FOAMS FOR
AEROSPACE APPLICATION

Dr. H. R. Moore

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Preliminary tests of one-part frozen urethane powders exposed in a high-altitude vacuum chamber operated at temperatures of -50° and 70° F have shown that a new group of triol-free branched polymers, esterified short of the critical degree of esterification, are capable of producing rigid foams with strength properties comparable to those obtained by high-temperature curing at atmospheric pressure. Controlled, reduced temperature, premixing of three categories of several two-part urethane systems, before rapid freezing in liquid nitrogen, was considered a significant factor in obtaining sufficient exotherm of isocyanate cross-linking reactions to initiate foaming in a low-temperature and vacuum environment.

THIS TECHNICAL NOTE WAS ADAPTED BY THE AUTHOR FROM A PAPER PRESENTED AT A SYMPOSIUM ON "MATERIALS AND PROCESSES FOR USE IN THE SPACE AGE," SPONSORED BY THE SOCIETY OF AEROSPACE MATERIALS AND PROCESS ENGINEERS, PHILADELPHIA, PENNSYLVANIA, 24 OCT 1960. THE OPINIONS EXPRESSED HEREIN DO NOT NECESSARILY REPRESENT THE VIEWS OF THE U. S. NAVAL AIR DEVELOPMENT CENTER.


DONALD MACKIERNAN
Technical Director

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TECHNICAL NOTE
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I N T R O D U C T I O N

This study is the first phase of a more comprehensive development program that should be undertaken to optimize materials and processing techniques in the manufacture of one-part frozen urethanes of possible use as rigidizing agents for low-cost, self-inflating, space vehicles. Major emphasis has been given the role of temperature control in the production of viscous urethane condensates before quick freezing in liquid nitrogen, with the view toward accelerating their expansion in a low-temperature and vacuum environment.

P R O P O S E D A P P L I C A T I O N S

Practically all the envisioned applications of one-part premixed urethanes are based on heat-sealing the freeze-arrested powders in double-wall, foldable, plastic film containers of widely varying configuration. Stehling¹ and Osgood² have surmised that urethane powders can be maintained in a frozen or semi-solid state in such enclosures for approximately 20 hours from the time of installation in the last stage of a rocket carrier to ejection of the folded payload in outer space. Voelker³ has attributed the anticipated rapid inflation of heat-sealed, double-walled structures to the instantaneous pressures exerted by residual air trapped in the heat-sealing operations, rather than to the ultimately higher foaming pressures exerted by previously injected, slow expanding, urethane powders in the hard vacuum of aerospace.

Figure 1 is a sectional view of a double-wall, heat-sealed, foam-rigidized toroid of uniform mechanical strength. Figure 2 is an artist's conception of the first and final stages in the outer-space fabrication of a low-cost, manned, space station embodying this construction. The astronaut ejected with the folded film package is quickly enveloped by the inflated toroid.

Since this work was completed, several companies have initiated programs on deep space applications of self-expanding polyurethanes.

1. Stehling, K. R. (Convair Division of General Dynamics), *Space Aeronautics* Vol. 34, No. 3, pp. 38, 45-47, Sep 1960
2. Osgood, C. C. (Astroelectronics Division of RCA), Preprint 60-68 of Paper Presented at Western National Meeting of the American Astronomical Society, 8-11 Aug 1960
3. Voelker, W. D. (Urethane Systems Engineering, Eikins Park, Pa.), Patent Application on Materials and Processes for Producing Self-Fabricating Space Stations

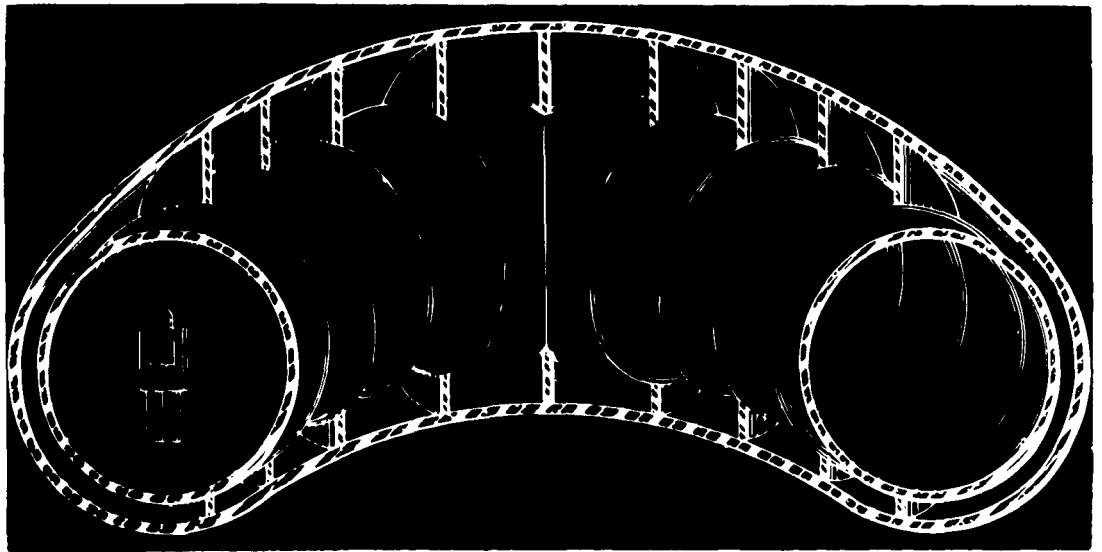


FIGURE 1 - Cross-section of the structure

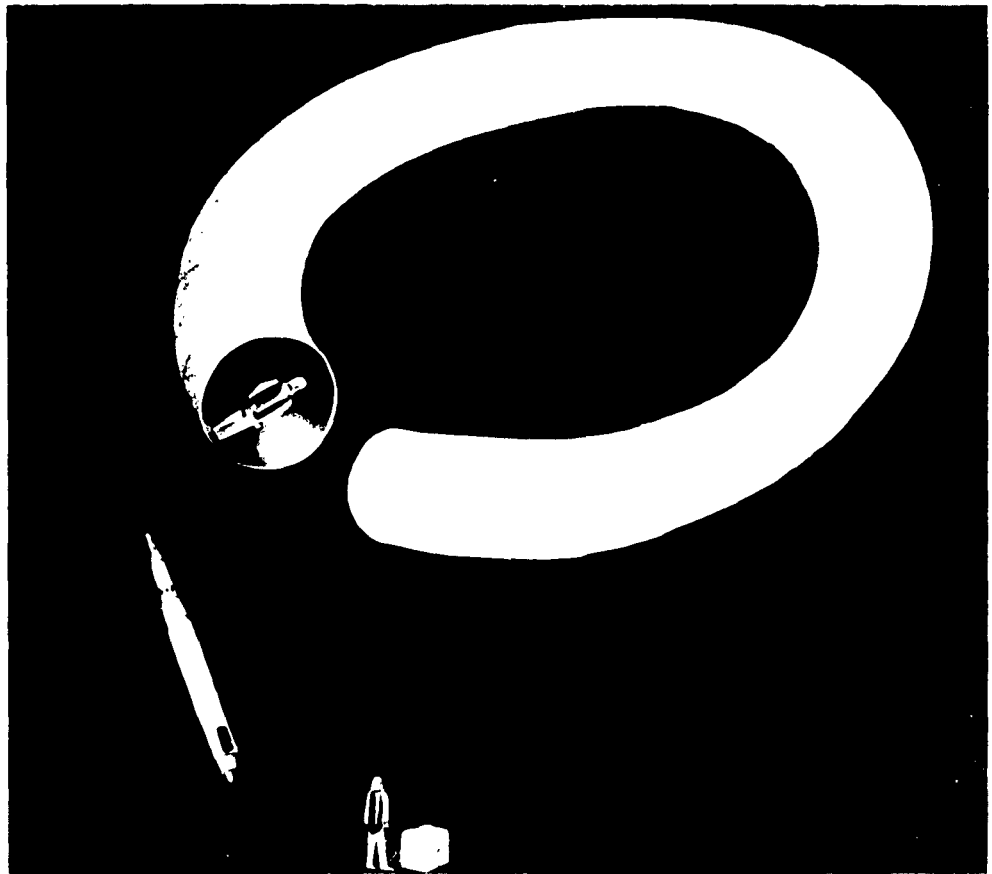


FIGURE 2 - A view of the structure from the side and the interior

Goodyear Aircraft Corporation^{4,5} has announced progress in utilizing one-part frozen urethanes as inflating and rigidizing agents for manned space stations 30 feet in diameter, light-weight solar concentrators to operate power systems in space, and various fabric structures with minimum launch penalty. Under Air Force sponsorship, the Aeronutronic Division of the Ford Motor Company⁶ is presently making a parametric survey of the possible applications of premixed polyurethanes for expandable aerospace structures. Stahler and Johnson⁷ have recommended their use for outer-space inflation of passive lens communication satellites.

Bilow of Hughes Aircraft Company⁸ has pursued an alternate, novel approach in synthesizing a wide variety of one-part "delayed action" polyurethanes not requiring freezing for deactivation. These linear urethanes reportedly are capable of melting and rigidizing space vehicles on exposure to the intensified ultraviolet radiation and heat of the sun in deep space⁹.

Reduction to practice of these contemplated uses is based on the assumption that the quantity of solar radiation transmitted through inflated plastic film enclosures is intense enough to counteract the intense cold of outer space and activate the frozen urethanes before temperature equilibrium is established. The adequacy of solar radiation in performing this task is supported by the maximum hot-spot temperatures, 307° to 349° F, calculated for the spherical, aluminized, Mylar satellite, Echo I¹⁰. Csgood² has recommended prior application of heat-absorbing surface coatings, heavily pigmented with carbon black or iron oxide, on the outer surface of plastic sheeting to intensify the effectiveness of transmitted solar energy in melting and foaming the enclosed urethane powder.

The feasibility of the plastic film concept of deploying low-cost orbiting vehicles in aerospace may well be resolved by tests of heat-sealed tubular structures containing frozen urethanes in the newly constructed environmental space simulator chamber designed by the Missile and Space Vehicle Department of the General Electric Company. The outstanding feature of this facility is the cylindrical, double-wall capsule shown in figure 3, 32 feet in diameter and 54 feet high, in which aerospace prototypes 20 feet in diameter can be tested after lateral

2. See page 1
4. *Government R&D Weekly*, Vol. 19, No. 10, 8 Mar 1961 issue of Federal Procurement Publications, Inc., Long Island City, N Y
5. Galloway, E. L. (Dow Chemical Co., *Chemical Engineering Progress* Vol. 57, No. 10, p 39, Oct 1961)
6. *Government R&D Weekly*, Vol. 19, No. 3, 18 Jan 1961, Contract No AF33(616)-7775
7. Stahler, Y. E. and Johnson, Lt. A. L. *Aeronautical Systems Command, WPAFB*, Technical Note No. TN 50-100, Mar 1961
8. Bilow, N. (Hughes Aircraft Company), Report No. P61-74, 15 May 1961, and succeeding quarterly reports under Contract No. AF33(616)-7925 sponsored by Aeronautical Systems Division, WPAFB
9. *Chemical and Engineering News*, 29 Jan 1962, pp. 48-49
10. Wood, G. P. and Carter, A. F., *NASA Technical Note TN D-115*, Oct 1959

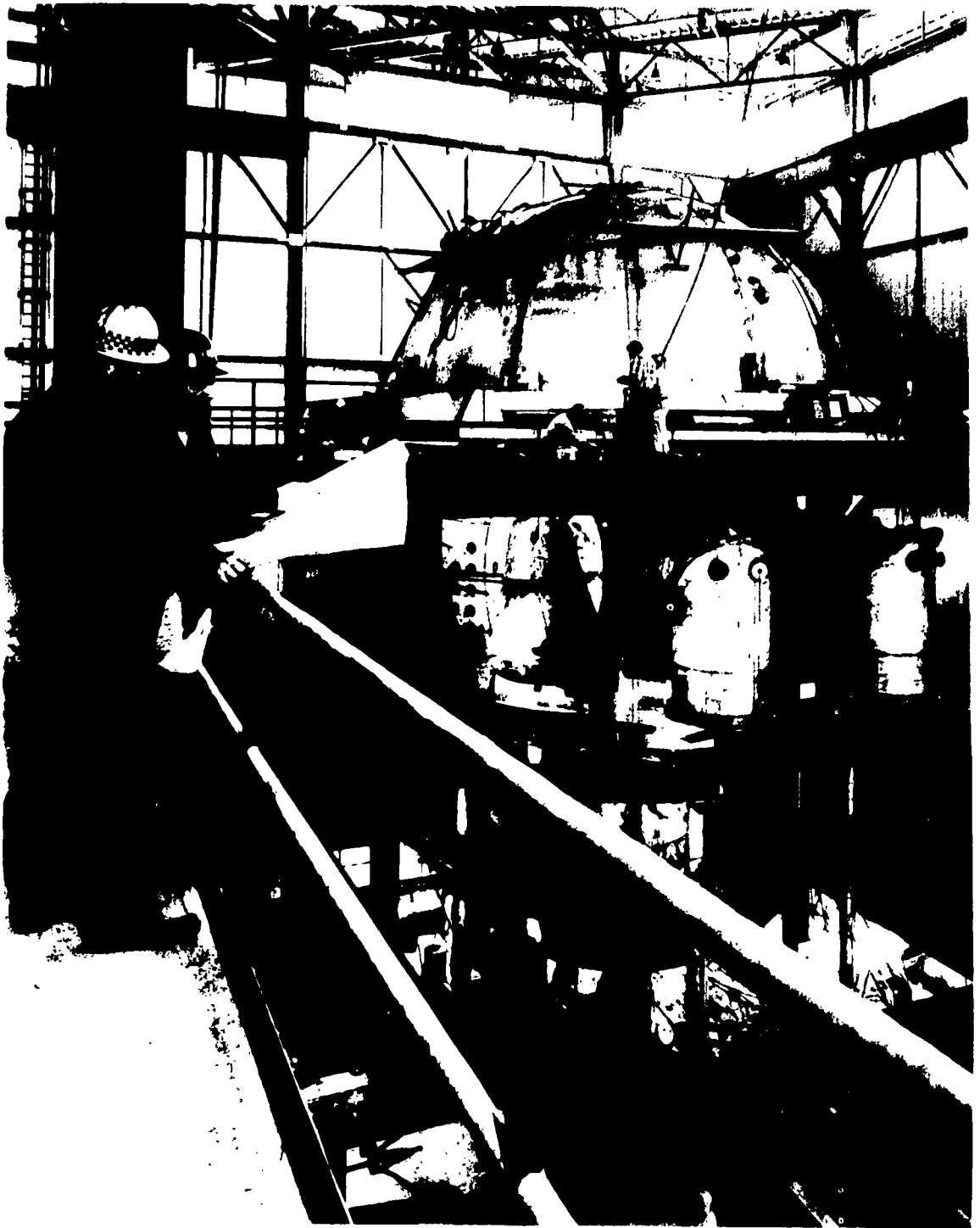


FIGURE 4-1. UNIT 1 REACTOR (4-1-1) (4-1-2)

displacement of the movable cap. Ducts in the side of the capsule are for connecting to the vacuum pumping system and banks of xenon lamps capable of irradiating test objects with a collimated light flux of the same intensity, 120 to 140 watts per square feet, and wavelength distribution of 0.25 to 3.0 microns, as solar radiation in outer space. Continued evacuation of the chamber with high-capacity pumps during progressive circulation of the liquefied gases, nitrogen and helium, through the double-wall interspace, provides a vacuum pressure of 10^{-3} mm of mercury and temperatures as low as -420° F.

P R I O R A R T

Unfortunately, little information is available in the technical literature on materials and methods of producing one-part frozen urethanes. Several years ago, Durst and Pace¹¹ obtained a patent on a method of freezing an alkyd resin-metatolylene diisocyanate (2,4-TDI) condensate, previously reacted to the threshold of incipient foaming, by cooling the outside surface of the reaction vessel with rapidly circulating acetone, refrigerated with dry ice. The claims to this process have emphasized the necessity of warming the outside surfaces of molds containing frozen condensate to initiate melting and expansion of foamed structures substantially free of air voids. Fisher and Gurney¹² evidently used this method in the foam encapsulation of closely spaced electronic components, since outside heat was required to initiate the foaming process.

In 1959 Moore¹³ described a method of preparing "heat-locked" frozen urethane briquettes capable of expanding spontaneously, within 45 to 60 minutes, to give rigid 8.0- to 12.0-pounds per cubic foot foams under normal laboratory conditions without applying outside heat. The critical factor in this low temperature control (LTC) process was the prolonged mixing of alkyd-2,4-TDI condensates, similar to those used by Durst and Pace, at reduced temperatures to imprison a large fraction of the total exothermic heat subsequently released in the formation of multiple polyurethane-amide and-urea cross-linkages in the expanded foam. A secondary factor was the sudden freezing of the viscous condensate accomplished by pouring the material quickly over a bed of dry ice to minimize the loss of exotherm.

E X P L O R A T O R Y S T U D Y

This preliminary work was undertaken with the object, first, of evaluating the adaptability of three categories of two-part urethanes, comprising: water and halogenated hydrocarbon (Freon-11) blown isocyanate

11. Durst, J. and Pace, H. A. (Goodyear Aircraft Corporation) U. S. Patent 2,706,311. 19 Apr 1955

12. Fisher, F. B. and Gurney, J. S. (Canadian Westinghouse Co.) Modern Plastics, Feb 1960, p. 218

13. Moore, H. R. (NAVYAIRDEVCON) U. S. Patent 2,889,291, 2 Jun 1959

pre-reacted prepolymer systems, 2,4-TDI-resinous compositions containing excess triol, and 2,4-TDI-triol free branched polymer condensates, to the low temperature and heat conservation process previously developed to upgrade the physical strength properties of rigid foams. Condensates responding favorably to low-temperature premixing schedules were frozen quickly in liquid nitrogen and then placed in a high-altitude chamber operated at a 2-centimeter pressure and a temperature of -50° F for observations of their free-foaming capability.

The role of low-temperature premixing was evaluated for three of the five qualifying two-part systems by conventional methods of no temperature control (NTC) and the Goodyear Aircraft Corporation process (GAC) of constant temperature control at 80° to 83° F to the end point of incipient foaming.

The environmental condition of a 2-centimeter vacuum at -50° F corresponds to an altitude of 80,000 feet and real kinetic temperatures of 31,000, 95,000, and 225,000 feet on the 1956 ARDC Model Atmosphere Chart. Ideally, the foaming tests should have been performed in a hard vacuum at much lower temperatures, both in the presence and absence of an intense source of radiation. However, it was felt that the tests without radiation might forecast a possible synergistic action of increased evolution of internal heat of cross-linking reactions in accelerating the expansion of surface-irradiated urethane powders in outer space.

PROCEDURES AND RESULTS

MATERIALS TESTED

Anticipating markedly improved free-foaming capability of "heat-locked" urethane powders at a 2-centimeter pressure due to the absence of the inhibiting force of atmospheric pressure, this study was limited to condensate formulations designed to give unrestrained, structural foams of 10-pound per cubic foot density under normal laboratory conditions. Listed in table I are seven two-part systems comprising three typical water and halogenated hydrocarbon-blown isocyanate prepolymers and semi-prepolymers, two older type alkyd resin-TDI systems, and two newly made triol-free branched polymer-TDI formulations.

Resins 400 and 500-2,4-TDI condensates, items 6 and 7 of table I, received the highest ratings in vacuum foaming tests at a temperature of -50° F. These resins were the only two viscosity stable polymers, based on the theoretical 1.5-to-1 hydroxyl-to-carboxyl starting molar functional group ratio, which could be converted to frozen one-part urethanes for reasons given in appendix A.

TABLE I

**IDENTIFICATION OF SEVEN TWO-PART URETHANE
FORMULATIONS SELECTED FOR TEST**

<u>Parts by Weight of Reactants</u>	<u>Type of Formulation</u>	<u>Producer</u>
1. Isofoam PE10A, 57.2 Isofoam PELOW, 42.8	Polyether prepolymer, waterblown	Isocyanate Products, Inc.
2. Rigidthane R334, 69.3 Rigidthane C334, 30.7	Polyether prepolymer, water and Freon-11 blown	Thiokol Chemical Corp.
3. PolyLite 8625 50.5 PolyLite 8605 49.5	Polyester semi-prepolymer, water and Freon-11 blown	Reichold Chemicals, Inc.
4. Nopcofoam A210R, 52 Nopcofoam A210T, 48	Branched polyester with excess triol	Nopco Chemical Co.
5. Selectron 5922 53 2,4-TDI, 47	Branched polyester with excess triol	Pittsburgh Plate Glass Co.
6. Resin 400, 50 2,4-TDI, 50	Branched polyester, triol-free	NAVAIRDEVGEN
7. Resin 500, 55 2,4-TDI, 45	Branched polyester, triol-free	NAVAIRDEVGEN

LOW-TEMPERATURE PROCESSING TECHNIQUE

The improvements in physical properties of structural foams obtained by this LTC premixing process has been ascribed to the effectiveness of low temperatures in suppressing the reactivity of the free hydroxyl groups in the resin to the degree required to permit a higher degree of completion of polyurethane, polyamide, and polyurea cross-linking reactions on cessation of cooling¹⁴. Exotherm was conserved at the pour point by the simple expedient of reducing temperature in the mixing process. This was done by maintaining temperatures only 1° to 2° F above the crystallization temperature of 2,4-TDI, 70° to 73° F, for the 2,4-isomer herein used in attaining single-phase compatibility, and thereafter continuing the mixing at preselected temperatures within the range from 40° to 70° F until an abrupt increase in condensate viscosity occurred. At this point, solid dry-ice additions were stopped and the reaction was allowed to proceed on its own exotherm with stirring until pour-point temperatures of 80° to 90° F were generated in the material, with accompanying sharp reductions in viscosity.

It was decided in this work to discontinue mixing the condensates at the instant of observing their characteristic abrupt viscosity increases, ranging from 850 to 2600 poises for the five approved formulations, rather than follow the usual procedure of sustained mixing, in the absence of temperature control, to obtain low pour-point viscosities of 100 to 400 poises. Theoretically, this departure from the standard procedure should conserve a higher fraction of the total potential heat of cross linking reactions in the frozen foam.

¹⁴. Moore, H. R., Office of Technical Services Report No. PB 131,123, 30 Jan 1956, 86 pp.

The operator in figure 4 is carefully adding dry-ice powder to reduce the temperature of a 600-gram batch of condensate in the 10-quart bowl of a Hobart planetary mixer. A copper-constantan thermocouple wire was soldered to the base of the bowl and connected to a potentiometer for instant readings of condensate temperatures. Mixing was interrupted at frequent intervals to determine condensate viscosities with a Brookfield viscosimeter, not shown.

Obviously this procedure, originally developed for the meta (2,4-) TDI isomer, is subject to considerable variation, depending upon the viscosity and diisocyanate reactivity of different branched resin formulations. In some cases, it was necessary to add 2- to 4-percent acetone on the weight of the batch to reduce excessively high pour-point viscosities. Desirably lower TDI compatibility temperatures, 47° and 58° F, can be obtained by substituting commercially available 65/35 and 80/20 2,4-/2,6-TDI isomer blends, characterized by freezing points of 46.4° and 57.2° F, respectively, for the higher freezing 2,4-TDI isomer containing not more than 2 percent of the 2,6-isomer.

REACTIVITY SCREENING TEST

Recent work¹⁵ has shown that highly viscous and extremely reactive foaming resins of controlled branching characteristics cannot be processed suitably by low-temperature TDI condensation processes. These tests have demonstrated a close parallelism between the time lag in the first evidence of decarboxylation under normal laboratory conditions without cooling, or by moderate temperature control at 85° F, and the ease with which two-part systems can be mixed at temperatures of 60° to 75° F by direct internal cooling with pulverized dry ice. For this reason, it was considered desirable to determine the threshold times of mixing and exothermic temperatures of the seven two-part formulations listed in table I before preparing sizeable batches for freezing and conversion to foam blocks in closed molds. Table II data, thus obtained without temperature control in mixing, show wide variations in elapsed times corresponding to the first discernible evidence of foaming, attainment of peak exotherm, and gradual cooling of the seven formulations to an arbitrarily preselected temperature of 122° F.

In these tests, the two-part systems were rapidly hand-mixed with a table knife stirrer to which a thermocouple, connected to the potentiometer, was attached. At the end point of incipient foaming, the knife was quickly removed and thermocouple readings recorded at successive 2-minute intervals until the fully expanded foams cooled to 122° F. Peak exotherm temperatures usually coincided with maximum expansion of the foams. The Rigidthane and Polylyte isocyanate prepolymer and semi-prepolymer formulations were rejected for large scale processing as a result of these tests, but the Isofoam water-catalyzed prepolymer was

15. Moore, H. R., O.F.S. Report No. PB 171,615, 22 Nov 1960, 73 pp.



considered a borderline case in view of its longer expansion threshold, 36 seconds, and 10-minute delay time in reaching a peak exotherm of 324° F.

TABLE II

EXOTHERMIC HISTORY OF 150-GRAM PITCHES OF URETHANE CONDENSATES
HAND MIXED WITHOUT TEMPERATURE CONTROL

Condensate Tested*	Expansion Threshold		Peak Exotherm		Elapsed Time (min) Cooling to 122° F	Density (lb/cu ft)
	Time (min)	Temp (°F)	Time (min)	Temp (°F)		
1. Isofoam	0.6	136	10.0	324	66	9.7
2. Rigidthane	0.3	210	1.5	249	30	9.5
3. Polylyte	0.3	198	3.2	354	62	9.2
4. Mopefoam	1.8	167	4.5	284	43	9.6
5. Selectron	13.5	165	18.0	279	58	10.5
6. Resin 400	6.0	180	14.0	310	63	8.3
7. Resin 500	3.2	198	10.0	324	67	14.1

* Based on proportions of reactants given in table I.

CONVERSION OF CONDENSATES TO FROZEN FOAMS AND FOAMED BLOCKS

Fixed amounts, 600 grams, of each of the five formulations, No. 1, 4, 5, 6, and 7, accepted by the reactivity screening test, were processed according to the time-temperature schedules listed by table III, columns 2 and 3. This quantity made adequate provision for transfer losses in pouring about 125 grams of condensate into a Dewar flask of 4300-milliliter capacity and 6-inches inside diameter, half filled with liquid nitrogen, and about 360 grams of the remaining material into a demountable aluminum mold of 8 by 10 by 1-1/2 inches inside dimensions, with the expectation of obtaining restricted foams of 10-pound per cubic foot density.

TABLE III

DENSITY AND COMPRESSION STRENGTH OF HEAT CURED RESTRICTED FOAMS
OBTAINED BY LOW TEMPERATURE PROCESSING

Condensate Tested*	Hobart Mixing Time (min)	Low Temp Range (°F)	Pour-Point Conditions		Foam Properties	
			Temp (°F)	Viscosity (ps)	Density (lb/cu ft)	Comp Strength (psi)
1. Isofoam	4.0	60-70	90	850	8.5	210
4. Mopefoam	10.0	60-70	95	1200	9.9	375
5. Selectron	30.0	68-70	90	1150	9.8	410
6. Resin 400	23.0	60-70	100	2600	7.4	235
7. Resin 500	11.5	63-70	98	1950	12.7	385

* Based on proportions of reactants given in table I.

Great care was required in the freezing operation shown in figure 5 to prevent undue sputtering and loss of liquid nitrogen. Condensate temperatures increased from 78° to 91° F in the 2- to 3-minute intervals required for freezing to appreciably higher temperatures, 90° to 100° F, on pouring 355- to 365-gram quantities of the remaining viscous materials into tared aluminum molds preheated to 150° F to avoid sudden chilling.

The same curing cycle of 1/2 hour at 150° F, followed by 3 hours at 275° F in an electrically heated air-circulated oven¹⁴ was used in preparing rigid foam blocks from which specimens were cut from center sections for density and compression strength determinations. The data given in table III represent the arithmetical means of density and compression strength given by five 1-inch cubes. A Tinius-Olsen electromatic tester, operated at a speed of 0.05 inches per minute, was used in measuring compression strengths of the cubes aligned perpendicular to the direction of foaming. The recorded values correspond to a deformation of 0.1 inch, or breakage of the specimens at this deflection, whichever occurred first.

It was noted that only two of the condensates, Nopcofoam and Selectron, gave restricted foams of about 10-pound per cubic foot density, while the Isofoam and Resin 400 condensates, in contrast, developed sufficient foaming pressure to force large amounts of material through the top channel member of the molds, with resultant low foam densities of 8.5 and 7.4 pounds per cubic foot respectively. Resin 500 condensate showed limited expansion under these conditions.

VACUUM FOAMING CAPABILITY

After first crushing 115- to 130-gram quantities of the frozen foams in cylindrical paper cartons, 3-1/4 inches in diameter and 6 inches high, in the presence of liquid nitrogen to prevent melting, they were promptly transferred to the high-altitude chamber shown in figure 6. Before evacuating the chamber, two thermocouples were introduced through a side opening and carefully inserted in the center area of each frozen powder. The side opening of the chamber was then sealed with a Thiokol-based elastomeric sealant.

The NAVAIRDEVGEN high-altitude chamber had a maximum vacuum and low-temperature capability of 8.3 millimeters and -100° F. Because of the difficulty in maintaining the urethane powders in the frozen state for the time required to obtain the minimum vacuum pressure, the tests were made at a substantially higher pressure, 2.0 centimeters, because of the rapidity with which this pressure setting could be obtained after arranging the test specimens.

To expedite the -50° F temperature setting, the chamber was precooled in advance. However, during the time interval required to attain a

14. See page 7

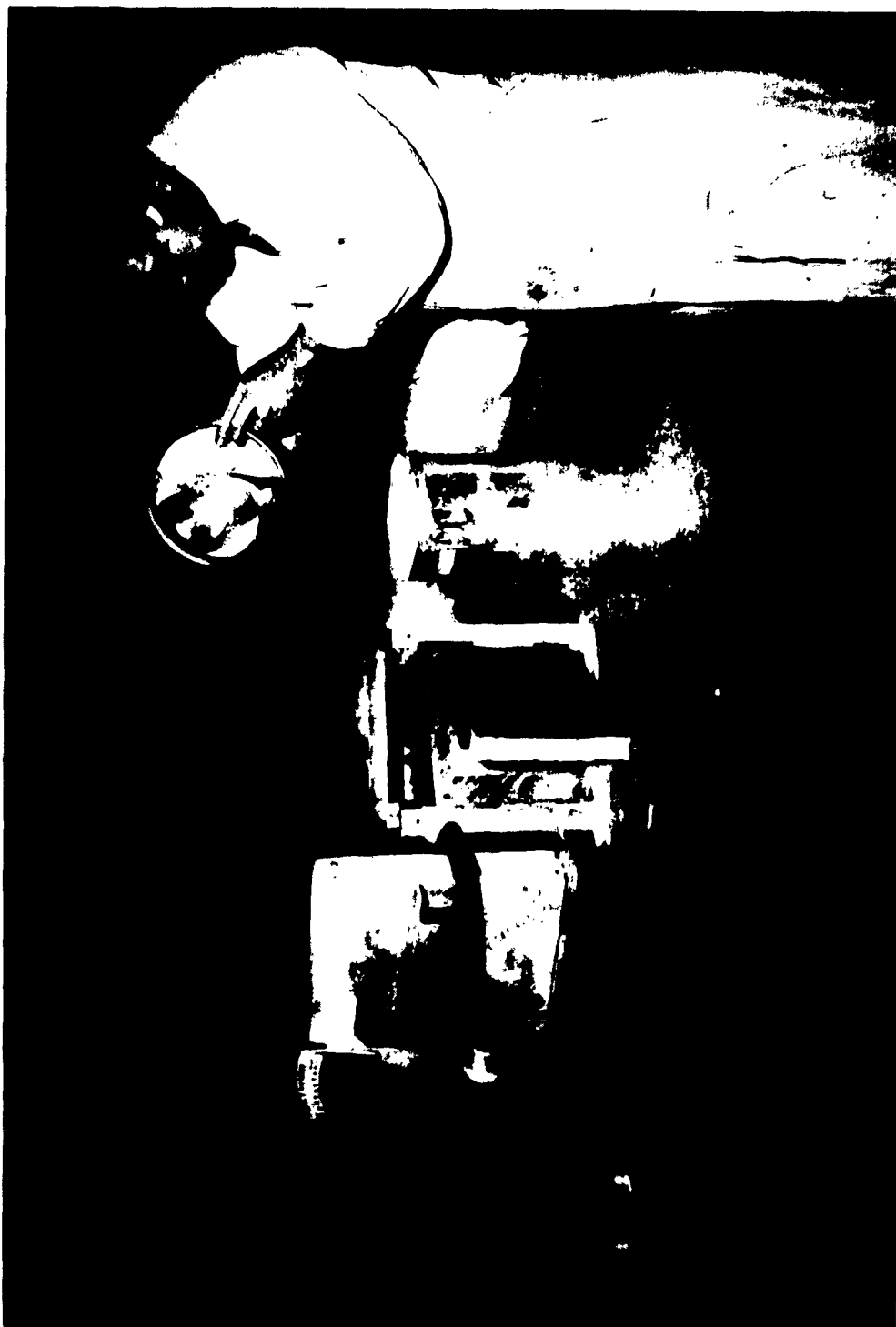


FIGURE 5 - Freezing Urethane Condensate in Liquid Nitrogen



FIGURE 6 - Inspecting Foams Expanded in Vacuo

vacuum of 2.0 centimeters, the temperatures of the frozen urethanes increased from their initial temperature, -324° F, the boiling point of liquid nitrogen, to temperatures ranging from -160° to -140° F.

Additional tests were made in vacuo at 70° F to determine the effect of a 2.0-centimeters vacuum on the properties of the Nopcofoam and Selectron powders previously found capable of expanding spontaneously, under normal laboratory conditions, after freezing over a bed of dry ice.

The vacuum foaming response of the Isofoam, Nopcofoam, and Selectron frozen condensates at 70° F, columns 9 and 10 of table IV, clearly established the merit of the LTC premixing procedure relative to control tests with condensates processed by NTC and GAC premixing methods of no temperature control and constant temperature control (80 – 83° F) to the end point of incipient foaming. The LTC-processed Nopcofoam and Selectron one-part urethanes filled the containers to overflowing, in sharp contrast to the negligible expansion given by other premixing methods. LTC-premixed Isofoam powder expanded to a lesser degree, as expected from the initial high loss of exotherm evolved in the manufacture of Isofoam PE10A prepolymer and all other categories of TDI prereacted polyols and hydroxylated resins¹⁶. The results obtained by LTC premixing of these three condensates clearly verified the prediction that conservation of a substantial fraction of the total exotherm of subsequent foaming and rigidizing cross-linking reactions in the frozen powder is advantageous in promoting vacuum expansion in the absence of a simulated source of solar radiation.

Table IV also shows that the rates of temperature increase given by thermocouples embedded in the frozen or semi-solid condensates for a 75° increment in temperature, from -125° to -50° F, were five to eight times as fast for condensates expanded in vacuo at 70° F as at -50° F. Three of the frozen powders, Isofoam at 70° F, and Nopcofoam and Resin 400 at -50° F, developed compression strengths only slightly less than the values recorded in table III in consideration of their differences in foam density.

Intermittent viewing of the quart-size cardboard containers through the double-wall glass window of the vacuum chamber disclosed wide variations in expansion times, ranging from 30 to 45 minutes for an environmental temperature of 70° F to 120 minutes at -50° F. Definitive measurements of the times and temperatures of initial expansion could not be made because of the opacity of the cartons. However, pronounced expansion of the LTC-processed Nopcofoam and Selectron frozen urethanes occurred when exotherms of only 17° to 20° F had developed after 25 to 34 minutes residence times in the vacuum chamber operated at 70° F. Expansion was essentially complete after a time lapse of 45 minutes, when foam temperatures had increased to 25° to 30° F.

16. *Encyclopedia of Chemical Technology, First Supplementary Volume*, Interscience Publishers, New York, 1957, pp. 894-897

TABLE IV

VACUUM FOAMING PERFORMANCE OF URETHANE CONDENSATES PULVERIZED
AFTER FREEZING IN LIQUID NITROGEN

Frozen Condensate Tested	Condensate Preparation Process Code*	Condensate Preparation		Rate Temp Increase		Temp Vacuum Chamber (°F)	Foam Properties		
		Mixing Time (min)	Pour Temp (°F)	-125° to Time (min)	-50° F per min Rate (°F)		Density (lb/cu ft)	Comp Strength (psi)	Texture
1a Isofoam	NTC	0.40	110	12	6.3	70	no ex- pansion		
1b Isofoam	LTC	4.0	85	6	12.5	70	6.3	105	medium; friable
1c Isofoam	LTC	4.0	85	51	1.5	-50	no ex- pansion		
2a Nopcofoam	NTC	1.4	95	20	3.7	70	collapses		
2b Nopcofoam	LTC	8.5	80	7	10.7	70	overflows		large voids
2c Nopcofoam	LTC	10.0	80	30	2.5	-50	14.9	230	medium
3a Selectron	GAC	28.0	95	15	5.0	70	collapses		
3b Selectron	LTC	30.0	86	6	12.5	70	overflows		large voids
3c Selectron	LTC	30.0	90	49	1.5	-50	no ex- pansion		
4 Resin 400	LTC	23.0	90	32	2.3	-50	6.6	180	medium
5 Resin 500	LTC	11.5	90	47	1.6	-50	11.3	450	fine

* Process Code

NTC - No temperature control in mixing to end point of incipient foaming.

LTC - Low temperature control by adding solid dry ice powder in mixing to end point of incipient foaming.

GAC - Goodyear Aircraft Corp. method of maintaining substantially constant temperatures of 80° to 83° F to end point of incipient foaming.

Table V data for the final specimen exposure time and temperature observations of the urethane powders are only approximate because of the difficulty in observing LTC-premixed condensates that failed to expand above the tops of the containers. No expansion was noted for observations bearing asterisks.

TABLE V

FINAL TIME-TEMPERATURE READINGS OF ONE-PART URETHANES

Frozen Condensate	+70° Chamber		-50° Chamber	
	Time (min)	Temp (°F)	Time (min)	Temp (°F)
Isofoam	60	77	90*	-34*
Nopcofoam	65	75	110	23
Selectron	75	80	120*	-15*
Resin 400	-	-	90	25
Resin 500	-	-	120	23

The terminal exposure times in vacuo at 70° F required to develop maximum exotherm of one-part frozen Nopcofoam and Selectron condensates, 65 and 75 minutes, were substantially greater than 45 to 60 minutes previously observed for the same LTC-premixed condensates expanding under normal laboratory conditions after freezing over a bed of dry ice.

D I S C U S S I O N

This preliminary study has indicated that LTC-premixed, freeze-arrested, urethane powders should qualify as acceptable rigidizing media for foldable, double-wall, plastic film structures, if the following conditions are satisfied:

1. Rocket delivery and orbital launch of the payload before melting and expansion of the enclosed powder.
2. Presence of a sufficient quantity of occluded air or lighter gas, such as helium, in the heat-sealed plastic film structures to insure rapid inflation without burst, on ejection from the last stage of a rocket carrier.
3. Capacity of the frozen or semi-solid material to expand rapidly in the gas-distended structure before temperature equilibrium is established in the hard vacuum and intense cold of deep space.

Aerospace expansion times of frozen or semi-solid urethanes can be markedly reduced by substituting higher melting refrigerants, such as dry-ice, for liquid nitrogen used in the present research. However, the use of higher melting refrigerants presupposes a marked reduction in the time interval between installation of the folded package in the rocket and blast-off, unless the payload itself is packaged in dry ice. In this case, it is believed that time lapses of 6 to 47 minutes, herein recorded for frozen condensates gradually increasing in temperature from -125° to -50° F, would be reduced significantly.

Despite the lack of experimental data on the behavior of frozen urethane powders in heat-sealed plastic tubes, it is believed that a correlation can be demonstrated between their capacity to fully inflate and rigidize the tubes, on the one hand, and their free-foaming capability at identical vacuum pressures and temperatures, on the other. High free-foaming capability is herein defined as the capacity of a given urethane powder to produce foams of density not exceeding 1.0 pound per cubic foot at temperatures ranging downwards from -50° to -100° F in vacuo.

Low-density foams are derived from one-part urethanes possessing high latent internal pressures. However, if the required internal pressures cannot be generated with existing or envisioned formulations, the deficiency can be readily overcome by injecting a sufficient excess of

powder into the tubes to produce foams of appreciably higher density, 2 to 4 pounds per cubic foot. Urethane powders capable of low-density expansion in this range would provide the necessary rigidizing effect, as high-strength properties obviously are not required in a weightless aerospace environment.

The foregoing analysis indicates that further work should be directed toward methods of developing high internal expanding pressures in frozen condensates. Two approaches are suggested in reaching this objective: (1) synthesis of new polyol-free branched polymers and branched polymer compositions containing a high concentration of sterically unhindered hydroxyl and carboxyl cross-linking sites, and (2) substitution of the low-melting 65/35 and 80/20 blends of TDI 2,4 and 2,6-isomers for the higher melting, 70-73.4° F, meta-(2,4-) tolylene diisocyanate isomer in producing LTC-premixed condensates capable of conserving still higher quantities of exothermic heat in the frozen foams.

Although it is recognized that further work on synthesis of polymers free from unesterified branching reactants is desirable, in view of the encouraging results given by LTC-premixed Resins 400- and 500- TDI condensates, this approach presents considerable difficulties because of the high initial viscosities of triol-free polymers. For this reason, the unmodified "Class I" and modified "Class II" diol chain-extended low viscosity, partially esterified, alkyd resin compositions, based on trimethylolpropane and 1,2,6-hexanetriol branching reactants present in excess of the amounts prescribed by the theoretical 1.5-to-1.0 hydroxyl-to-carboxyl starting molar function group ratio, should be investigated¹⁵. The presence of unesterified branching reactants of this type, possessing equal hydroxyl reactivity, is not believed deleterious in the light of the much higher exothermic temperatures, 425° to 500° F, given by these triols after 25 minutes of mixing with 2,4-TDI in equimolecular proportions, as compared to 97° F for anhydrous glycerol.

Lastly, the results of this study have shown that no further work is indicated for water and halogenated hydrocarbon-blown isocyanate prepolymers or semi-prepolymers in consideration of the pronounced loss of exotherm released in the original manufacturing process¹⁶. Nor can these materials, stirred in vacuo at 70° F, be foamed satisfactorily unless the aqueous catalyst is introduced at an extremely slow rate by desorption from silica gel. Allinikov¹⁷ has concluded that elaborate arrangements of this sort are impracticable for unrestrained free-foaming of shelters and observatories on the moon, even if heating means were provided to overcome their excessive viscosities in an aerospace environment.

15. See page 8

16. See page 14

17. Allinikov, S. (Aeronautical Systems Command, WPAFB), Technical Memorandum WWRCE TM 60-4, 28 Jun 1960

A C K N O W L E D G E M E N T

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H. R. Moore

H. R. Moore

A P P E N D I X A

PREPARATION AND PROPERTIES OF TRIOL-FREE BRANCHED POLYMERS

INTRODUCTION

Triol-free branched polymers were produced for this research by condensing various triols (glycerol, trimethylolpropane, 1,2,6-Hexanetriol) with dibasic organic acids in equimolecular proportions corresponding to a 1.5-to-1 hydroxyl-to-carboxyl starting functional group ratio. This ratio corresponds to the maximum amount of triol that can be fully incorporated in a branched polymer depicted by the configuration

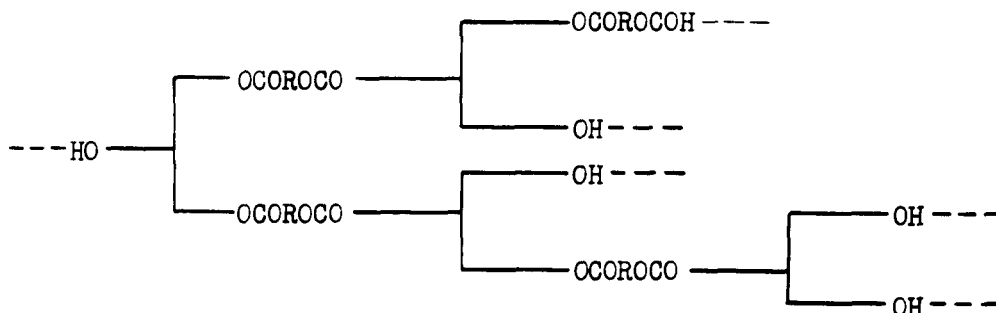


FIGURE A-1 - Schematic Structure of Polymer Based on the Condensation of Four Moles of Triol with Four Moles of Dibasic Acid Bearing Only One-Terminal Carboxyl Group

The broken lines in the figure represent the sites for further condensation reactions terminated by cross-linking of adjacent molecules and gelation of the mass when the acid number is reduced to a critical value.

VERIFICATION OF BRANCHED STRUCTURE

The decision to prepare a family of triol-free polymers containing one terminal carboxyl group was based on the confirmation of previous observations¹ that two lots of Selectron 5922, characterized by acid numbers 46 and 40, contained 8.3 and 7.7 percent unreacted glycerol. These results represented the summation of the glycerol contents of 3 water extracts of 100-gram samples of the resins placed in a Waring blender. The glycerol assay of the extracts was determined by titrating the formic acid liberated by oxidation with sodium periodate in accordance with the procedure developed by Dal Nogare and Oemler². The

1. *ONR Publication ONR-5; Materials Research in the Navy*, by H. R. Moore; Vol. 1, pp 19-67, Mar 1959

2. *Dal Nogare and Oemler, Analytical Chemistry*, Vol. 24, pp 902-904, 1952

presence of glycerol was verified by expelling acrolein from concentrated water extracts containing potassium hydrogen sulfate to aid the dehydration.

A compelling reason for synthesizing triol-free polymers was the observation that pure glycerol, water-free, generated a peak exotherm of only 97° F after 25 minutes of hand-mixing, with 2,4-TDI added in equimolecular proportions. This result indicated that the relatively small amounts, 8 to 9 percent of free glycerol present in Selectron 5922, would reduce the effectiveness of LTC premixing in conserving the optimum quantity of exothermic heat of cross-linking reactions in frozen foams. This prediction was borne out by the lower peak exotherm of 279° F recorded for hand-mixing Selectron 5922-TDI condensates, as compared to 324° F obtained for Resin 500-TDI mixtures. This may account in part for the inferior vacuum-foaming performance of Selectron 5922 relative to Resins 400 and 500. It is likely, also, that Nopcofoam A210R branched resin composition is a "Desmophen" triol-containing resin³.

Selectron 5922 was made, as explained by Pace⁴, by condensing 3.8 moles of glycerol with 2.5 and 0.5 moles each of adipic acid and phthalic anhydride at temperatures of 390° to 400° F, until resinous compositions with acid numbers of 46 to 40 were obtained. In this work it was found that continued polymerization of both the commercial product and a duplicate formulation, based on the same 1.9-to-1 OH-to-COOH starting functional group ratio, until acid numbers of 2 to 3 were attained, gave extremely high viscosity resins containing less than 1 percent glycerol. These results confirmed the statement in Groggins⁵ that free triol present in partially esterified alkyds of this type eventually combines with carboxyl end groups to give molecular structures similar to that shown in figure A-2, wherein all the terminal groups are hydroxyl.

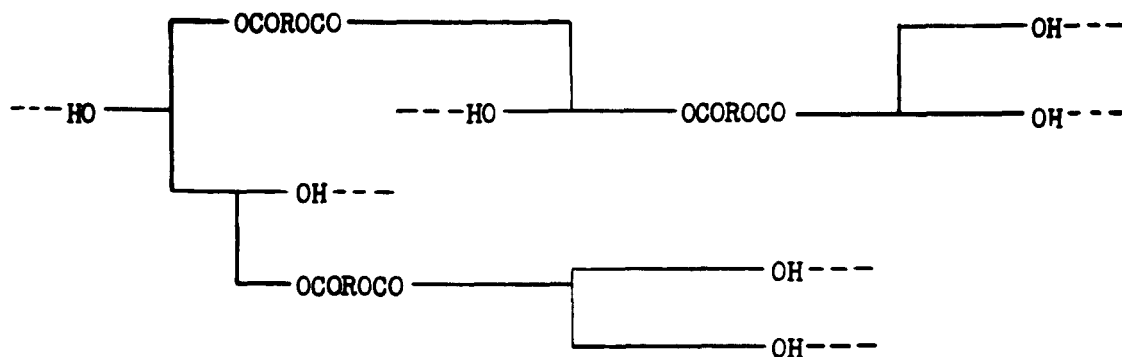


FIGURE A-2 - Schematic Structure Containing No Free Carboxyl Groups

3. Simon, E. and Thomas, F. V.; U. S. Patent 2,577,281, 4 Dec 1951

4. Pace, H. A.; OTS Report No. PB 110497, Dec 1949

5. Groggins, P. H.; *Unit Processes in Organic Synthesis*; McGraw-Hill Book Company, Inc., New York, Fifth Edition, 1958, p 863

Figure A-2 configuration is an oversimplification of the actual and more highly branched structures, containing at least 50 esterified triol molecules, undoubtedly resulting from excessive polymerization of triol and dibasic acids reacted in proportions corresponding to a 1.875-to-1 OH-to-COOH molar starting functional group ratio.

RESIN PREPARATION

Listed in table A-I, column 2, are the molar proportions of polyfunctional reactants used in producing 750- to 850-gram quantities of 6 triol-free polymers, Resins 100-600, inclusive.

A 2-liter beaker placed in an electrically heated fiberglas mantle served as the reaction vessel in preparing the resins. Esterification temperatures were controlled with a variac, and tank nitrogen was aspirated continuously into the beaker during the progress of the condensation reactants. Reaction times and temperatures varied between the limits of 3 to 13 hours and 180° to 370° F, respectively.

Columns 3 and 9 of the table give the final acid numbers and Brookfield viscosities of samples removed for test while the resins were still warm, but after stopping the condensation process. In this connection, it was noted that only two of the formulations, Resins 400 and 500, gave stable acid values and viscosity readings; the remaining resins, 100, 200, 300, and 600, gelled within 24 to 168 hours from the time of preparation. For this reason, the experimental observations and the analytical criteria based on the initial acid numbers of these resins have been enclosed in parentheses.

ANALYTICAL PARAMETERS OF TRIOL-FREE POLYMERS

A significant difference between triol-free and triol-containing polymers is the marked gelation tendencies of the former, which occurred on attaining acid numbers as high as 50. However, the incidence of gelation of triol-free polymers on approaching acid numbers corresponding to 86.6 percent degree of polymerization is appreciably less than 75 to 79.5 percent reported by Kienle and co-workers⁶, for similar formulations based on a 1-to-1 starting functional group ratio. The 1-to-1 function group analog of the polymer shown in figure A-1, herein depicted as figure A-3, containing equal numbers of free hydroxyl and carboxyl groups, cannot exist because the calculated degree of esterification, 80.6 percent, exceeds the maximum gelation threshold of 79.5 percent.

Figure A-4 represents a segment of the cross-linked gel evidently obtained by excessive condensation of polyfunctional reactants in proportions corresponding to functional group ratios both equal to, and less than, 1.5-to-1.

6. Kienle, R. H. and co-workers; *J. Am. Chem. Soc.* 61,2258,2268 (1939); 62,1053 (1940); 63,481 (1941)

T A B L E A - I

POLYFUNCTIONAL REACTANTS, ANALYTICAL AND STRUCTURAL PARAMETERS OF TRIOL-FREE BRANCHED POLYMERS

Resin No.	Materials (moles)	$\overline{AN_p}$, Obsd	P_c (%)	$\overline{W_p; x_p}$	$\overline{AN_{pg}}$	$\overline{W_{pg}; x_{pg}}$	h_p	Viscosity (ps) at 72F	Branching Coeff; α
100	Glyc 3.0 Ada 2.5 PAA 0.5	(49.5)	(89.2)	(1133; 5.5)	63.0	890; 4.4	(331)	76,800 (gel)	0.53
200	Glyc 3.0 Seba 3.0	(45.5)	(88.0)	(1231; 4.7)	51.1	1096; 4.2	(267)	22,400 (gel)	0.52
300	TMP 3.0 Seba 3.0	(27.1)	(91.8)	(2070; 6.8)	44.7	1254; 4.2	(218)	40,200 (gel)	0.56
400	Hexol 3.0 Ada 3.0	60.9	84.8	922; 3.8	53.6	1043; 4.2	292	2,300	0.48
500	Glyc 3.0 Ada 3.0	66.3	85.9	847; 4.1	63.2	888; 4.3	348	5,200	0.49
600	TMP 3.0 Ada 3.0	(49.9)	(87.6)	(1123; 4.5)	53.6	1046; 4.2	(286)	17,300 (gel)	0.51

MATERIALS: Glyc, glycerol; TMP, Trimethylolpropane; Hexol, 1,2,6-Hexanetriol; Ada, Adipic acid; PAA, phthalic anhydride; Seba, Sebacic acid

SYMBOLS: $\overline{AN_p}$ - Observed acid number of polymer
 P_c - Percentage esterification of carboxyl group equivalents initially present
 $\overline{W_p; x_p}$ - Average molecular weight and average number of branch points at attained acid number
 $\overline{AN_{pg}}$ - Theoretical acid number corresponding to incipient gelation
 $\overline{W_{pg}; x_{pg}}$ - Theoretical average molecular weight and average number of branch points at incipient gelation
 h_p - Hydroxyl number of polymer at attained acid number

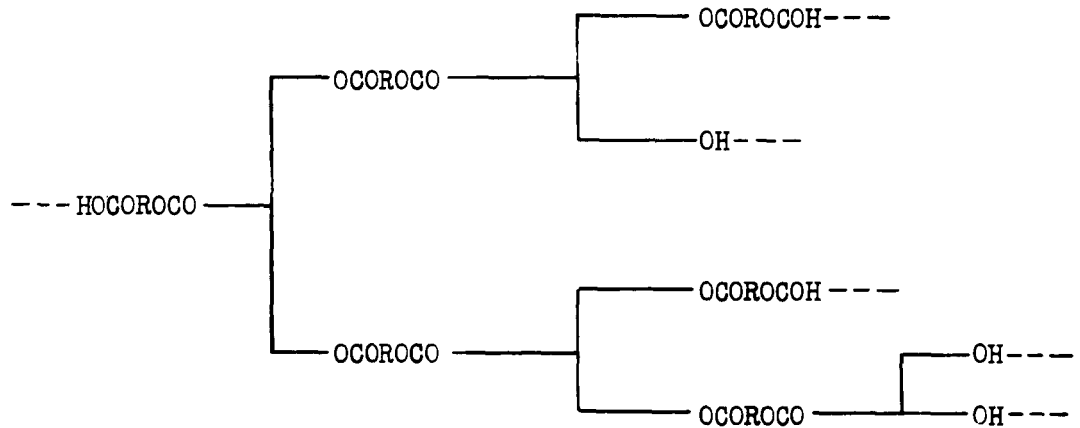


FIGURE A-3 - Hypothetical Structure of Polymer Based on the Esterification of 4 Moles of Triol by 6 Moles of Dibasic Acid

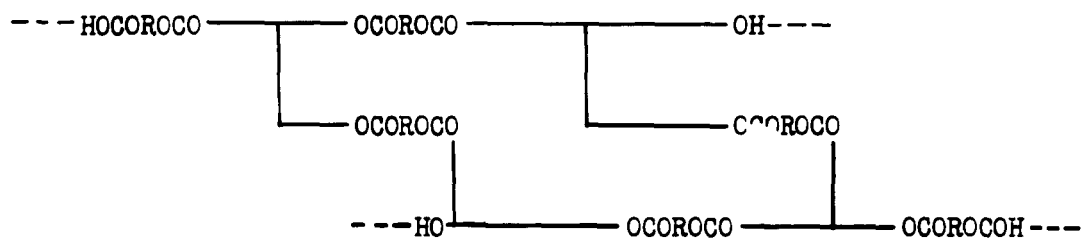


FIGURE A-4 - Segment of Gelled Polymer Based on Triol Branching Reactant

The foregoing discussion indicates that the critical factor in synthesizing viscosity-stable and triol-free polymers is the degree of polymerization and acid numbers corresponding to the incidence of gelation reactions. The starting point in these calculations is Flory's basic equation⁷,

$$\alpha = P_c^2 / r \quad (1)$$

for determining the branching probabilities, α , of unmodified, diol-free polymers. P_c in this equation is the percent esterification of the carboxyl group equivalents initially present in the starting formulation.

For the special case where r is 1.5 and α becomes α_c , 0.500 for triol-based polymers, P_c is equal to P_{cg} , the critical degree of esterification corresponding to the gelation threshold. The numerical value

7. Flory, P. J.; *Principles of Polymer Chemistry*; Cornell University Press, Ithaca, New York, 1953, pp 348-356

of P_{cg} is then 0.866, or 86.6 percent, obtained by writing equation (1) in the form

$$P_{cg} = \sqrt{a_{cr}} \quad (2)$$

This value of P_{cg} is fixed and independent of the total weight in grams, W_1 , of the reactants present in the initial charge.

The limiting values of the acid numbers of the polymers corresponding to the gelation threshold are inversely proportional to the weight of initial charge, as shown by writing the generalized equations

$$P_c = \frac{(45000 N_c/W_1) - 0.802 AN_p}{45000 N_c/W_1}, \quad (3)$$

previously derived for calculating the percent esterification of alkyd resinous compositions of controlled branching coefficients⁸ in the form

$$AN_p = \frac{(1 - P_c) 45000 N_c}{0.802 W_1}. \quad (4)$$

Substituting P_{cg} for P_c and AN_{pg} for AN_p , equation (4) becomes

$$AN_{pg} = \frac{(0.134) 56100 N_c}{W_1}. \quad (5)$$

The number of carboxyl equivalents, N_c , is 6 for Resins 100-600, inclusive, and 56100 is the number of milligrams of 0.1N KOH required to neutralize one carboxyl equivalent.

In further reference to table A-I, it is evident that Resins 400 and 500 were the only two polymers condensed to a lesser degree than 86.6 percent. Their acid numbers also were appreciably higher than the AN_{pg} maximums, 53.6 and 63.2, corresponding to the start of network formulation.

Due emphasis should be given the fact that the numerical values of P_c , AN_{pg} , and h_p listed in columns 4, 6, and 8 of the table are independent of any assumptions concerning the branched structure configurations and average molecular weights of the polymers. However, the computations of weight average molecular weights, W_p and W_{pg} , and the corresponding average numbers of esterified triol molecules ("branch points"), x_p and x_{pg} , tabulated in columns 5 and 7, are predicated on figure A-1 concept of triol-free branched structures bearing only one terminal carboxyl group.

8. Moore, H. R.; OFS Report No. PB171615, 26 Nov 1960, 73 p

Presuming on the validity of this concept, the acid numbers attained from weight average and the acid numbers corresponding to gelation thresholds were calculated from the equations

$$W_p = \frac{45000 \times 1.245}{AN_p} \quad (6)$$

$$W_{pg} = \frac{45000 \times 1.245}{AN_{pg}} \quad (7)$$

where 1.245 is the KOH/COOH conversion factor. Equations (6) and (7) are substantiated by the definitions of corresponding acid numbers given by equations (4) and (5).

An alternate method of determining W_p and W_{pg} and the corresponding average numbers of branch points, x_p and x_{pg} , is provided by curves of the type shown in figure A-5 for Resin 500, wherein W_p values for whole numbers of x_p as ordinates are plotted against decreasing values of AN_p as abscissas. The numerical values of W_p for integral values of x_p from 3 to 6 were obtained from the equation

$$W_p = x_p W_1 - (2 x_p - 1) 18.016 \quad (8)$$

Equation (8) is consistent with figure A-1 which shows that the weight of water evolved in producing polymers with a specified number of branch points is equal to the product of twice the number of partially esterified triol molecules in the polymer, less one, and the molecular weight of water. Acid numbers corresponding to increasing values of W_p were then obtained from equation (6) written in the form

$$AN_p = \frac{56100}{W_p} \quad (9)$$

The fractional numbers of branch points, x_p and x_{pg} , for the observed and calculated values of AN_p and AN_{pg} are given by the ordinate intercepts of the curve obtained by plotting W_p against AN_p for whole number values of x_p .

Obviously, the broken line continuation of this curve beyond the point given by the AN_{pg} and x_{pg} intercepts of 63.2 and 4.3 cannot be realized in practice because of the intervention of gelation cross-linking reactions between polymers containing 4.2 and 4.4 partially esterified triols.

Tabulated in column 8 of the table are the hydroxyl numbers of the polymers required, in addition to acid numbers and residual water content, for determining the minimum amounts of TDI needed for their conversion to foams in accordance with stoichiometric principles. Here again, the values given by the equation

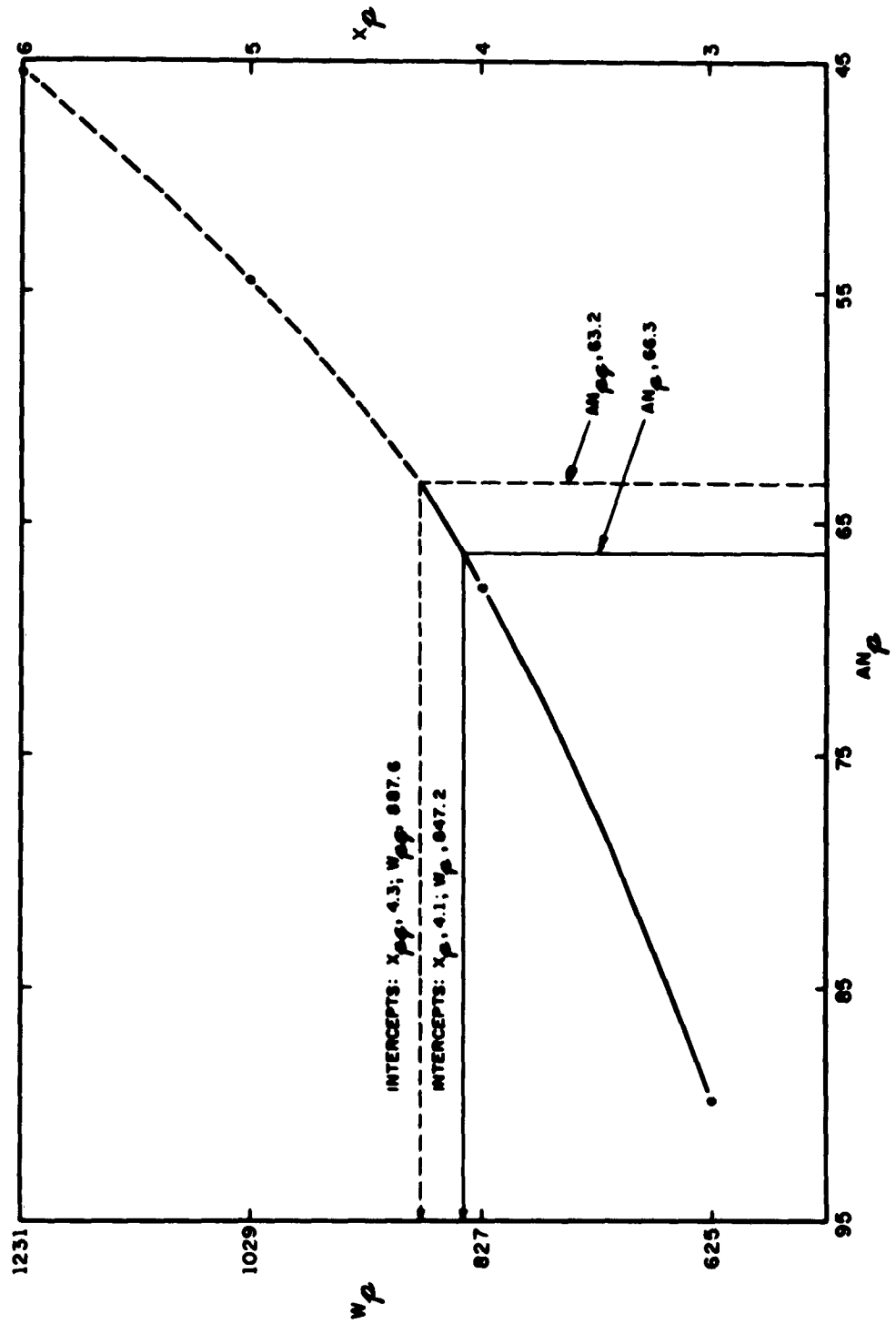


FIGURE A-5 - Weight Average Molecular Weight and Branch Points of Resin 500 at Attained and Minimum Acid Numbers

$$h = \frac{(N_h - P_c N_c) 17000 \times 3.3}{W_1 - 18.016 (P_c N_c)} \quad (10)$$

are provisional for Resins 100, 200, 300, and 600, because of gelation reactions that occurred at varying times after the resins were prepared.

The free hydroxyl group content of the polymers is clearly equal to the number of unesterified hydroxyl equivalents per unit weight of product. The term $N_h - P_c N_c$ in the numerator of equation (10) represents the number of unreacted hydroxyl equivalents in consideration of the identity

$$P_h N_h \equiv P_c N_c \quad (11)$$

where P_h is the percentage esterification of the number of hydroxyl equivalents, N_h , initially present. Weight of product is given by the difference between the weight of the initial charge in grams, W_1 , and the product $18.016 P_c N_c$, since 1 molecule of water is liberated for each esterified carboxyl equivalent.

The residual water of esterification present in Resins 400 and 500 was not determined. However, on the basis of previous results given by Moore⁸, a reasonable value, 4 percent, was assigned the water content of these resins. On this basis, the arbitrary 1-to-1 and 0.82-to-1 TDI-to-resin ratios selected in converting Resins 400 and 500 to frozen foams were 17 and 9 percent in excess of the theoretical values. An excess of TDI was considered justifiable on the assumption that an excess is less harmful than a deficiency in frozen condensates subjected to a low-temperature vacuum environment.

Lastly, column 10 of the table shows that the branching coefficients of Resins 100, 200, 300, and 600, esterified in excess of the critical value, 86.6 percent, were greater than 0.500, the critical value for production of infinite networks, as expected.

CONCLUSION

In the further development of triol-free intermediates for the preparation of LTC preprocessed condensates, care should be taken to limit the degree of esterification of carboxyl group equivalents initially present to 82 percent, or less, to obtain products of substantially lower viscosity than 2600 poises recorded for Resin 400. Low viscosity resins obviously would be more amenable to TDI condensation reactions performed at 48° to 58° F with the low melting point 80/20 and 65/35 2,4- and 2,6-isomer blends.

An effort also should be made to expell all traces of the residual water of condensation by aspirating nitrogen through the resins at

8. See page A-6

temperatures of 200° to 225° F, believed to be incapable of further advancing the condensation reactions. Removal of residual water by vacuum distillation at temperatures of 150° to 175° F might be found even more effective.

The presence of water in triol-free and triol-containing resins is undesirable because of the preferential formation of linear polyureas in TDI condensation reactions. Prior formation of polyureas in this way causes an undesirable increase in the viscosity of the condensates at low temperatures, thus aggravating the processing difficulties. Moreover, the presence of linear polyureas in the expanded foams depreciates their mechanical strength properties to a marked degree^{8,9}.

8. See page A-8

9. Moore, H. R.; OIS Report No. 131123, 30 Jan 1958, 86 p

U. S. Naval Air Development Center, Johnsville, Pa.
Aeronautical Electronic and Electrical Laboratory
TECHNICAL NOTE, URETHANE FOAMS FOR AEROSPACE APPLICATION: by H. R. Moore; 2 Mar 1962 : 29 p; Report No. NADC-EL-N6208

Preliminary tests of one-part frozen urethane powders exposed in a high-altitude vacuum chamber operated at temperatures of -50° and 70° F have shown that a new group of triol-free branched polymers, esterified short of the critical degree of esterification, are capable of producing rigid foams with strength properties comparable to those obtained by high-temperature curing at atmospheric pressure. Controlled, reduced temperature, premixing of three categories of several two-part urethane systems, before rapid freezing in liquid nitrogen, was considered a significant factor in trapping sufficient exotherm of isocyanate cross-linking reactions to initiate foaming in a low-temperature and vacuum environment.

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